Master's Thesis for Graduate School of Human Ecology

DEVELOPMENT OF A SUPERHYDROPHOBIC DIGITAL-PRINTED COTTON FABRIC

초소수성 디지털날염 면직물 개발

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Abstract

A superhydrophobic digital-printed cotton fabric has been developed by the dip coating method to find applications in the apparel and textile industries due to the exposure of apparel and textiles products to the environment regarding water-repellency and self-cleaning abilities.

The microstructure and surface morphology of the prepared digital-printed fabrics was examined using the scanning electron microscopy. Fabrics proved breathable based on the air permeability of the prepared samples. Evaluation of coating durability of the modified digital-printed fabric was by a washing method.

This revealed the durability and self-healing properties of the treated digital-printed cotton fabric after heat-treatment with water contact angle at 156$^{\mathbf{o}}$ lower than the water contact angle recorded before the evaluation of coating durability at 162$^{\mathbf{o}}$.

The water shedding angle for the developed digital-printed fabric could not be recorded due to the stickiness of the surface of the treated digital printed cotton fabric which produced an angle above the accepted angle at 10^{o}. Therefore, this technique produced a digital-printed fabric with double functionalities of water-repellency and self-healing properties and could be used in the apparel and textiles industries especially for fashion accessories.

Keywords: Superhydrophobic, Digital-printed Fabric, Water contact angle, Self-healing, Repellent, Durable

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Introduction

1.1. Necessity of study

Cotton fabrics and apparels with special wetness and self-cleanable characteristics have evoked a large amount of quality of curiosity in experimentation and practical fields. This is due to new researches of superhydrophobic fabrics in the apparel and textile industries. These applications are ‘self-cleaning [1]’, ‘oil and water separation [2]’ and ‘water repellency [3]’.

Superhydrophobic surfaces have mainly been concentrated on pristine fabrics. Recently, few studies have revealed superhydrophobicity on dyed or printed fabrics. However, to be used in the apparel and textile industries, dyeing or printing is essential for the fabrics.

It is therefore necessary to develop a method to impart superhydrophobicity to the dyed or printed fabrics; hence this research to develop a digital-printed cotton fabric having superhydrophobic and self-healing properties by the application of non-fluorinated zirconium nanoparticles using the dip coating method. Besides, the treated digital-printed cotton fabric samples were to be compared with only the treated cotton fabrics to examine the bonding mechanism between the reactive pigment and the non-fluorinated hydrophobic reagents in figure 1.

The developed fabric had self-cleaning functionalities since self-cleaning mechanisms have been reproduced after the lotus leaves with less surface-energy substance and surface features which are dependent on the surface roughness to acquire a water-repellent uppermost layer [4], colour fastness with other practical usages in the apparel and textile environment.

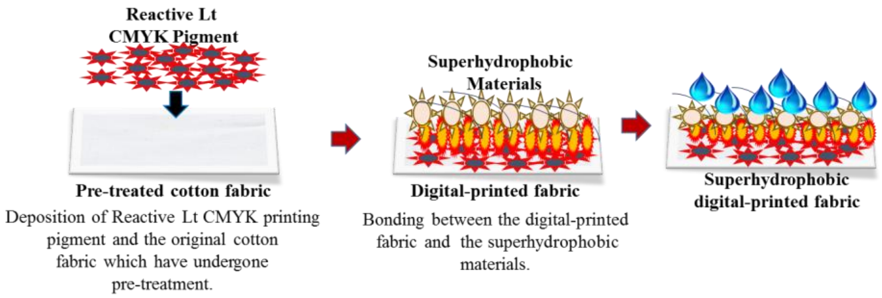


Figure 1. Mechanism of surface treatment of digital-printed fabric

1.2. Theoretical background

1.2.1. Digital printing

The interests in ink-jet printing on textile surfaces have increased in academic and industrial fields. Some benefits of ink-jet printing include customization, high speed, cleanliness, flexibility, substrate independency and to integrate with existing production lines [5]. Digital printing machines were first designed for printing on papers. Meanwhile, inkjet printing technology is accepted now into the fabric printing market than before since it has met the needs of the new apparel and textile market [6].

The cotton fabric has been identified as the most widely used natural textile fibre in the world and commonly printed by the reactive dye-based ink.

Reactive inks used in ink-jet machines commercially are relied on the dyes that possess low to moderate fixing properties generally ‘mono-functional’ reactive pigments [7].

Pre-treatment processes are very important when printing with reactive dyes and digital printing machines to increase the colour yield. This is done by a ‘one-bath’ treatment done before printing with sodium alginate, glycidyl trimethylammonium chloride (GTA), urea and sodium hydroxide. This has been designed for ‘sizing’ and ‘cationization’ of the fabric before printing [8]. This is done because of the common use of reactive dye-based inks for the printing of cotton and some cellulosic fibres/fabrics that result to their shade range with very good and desired fastness properties.

Since, reactive dyes have very little reactivity with the chemical reaction of the reactive groups with water when dye fixation is being carried out; the dyes possess a fixation ranging from 50-80%. This results in generating a large amount of wastewater of the dye [9]. After digital printing with reactive dyes, a post-treatment is done with steam fixation, washing-off and drying.

In addition, pigments are used without any difficulty and are the most frequent colorant employed in textile printing [10]. The following are some of the factors considered when choosing a component for a pigment to be used in an ink jet digital printing [11]:

- Pigment dispersion which gives the colour.
- A polymeric binder which is a mixture of polymers for image durability for a longer time.
- Water as a necessity to be used to convey the aqueous inkjet inks to be carried to other components.
- A co-solvent aside water was used to aid the water convey other ingredients used through solubility and compatibility. This enhances the performance of the elements that helps in the wetting and sticking of the ink to the fabrics and substrates.
- Surfactants were used as nozzle and surface wetting to help the ink flow out in great quantities for reliability and stabilization of the key ingredients used. These helps the key ingredients mentioned ‘binder and pigment particles’ from becoming compact at only few points.
- Substances added to other substances ‘humectants’ present in the pigment aids to prevent drying when printing is not in process.
- Defoamer ‘antifoam’ is also used as an agent to reduce foaming.
- A sticky-control agent is also considered to control the destroying of the pigment and formation of droplets.
- A substance as a penetrating speed drying property on substrates such as on paper and textile.
- An antibiotic/biocide is also used to avoid fabrics from bleeding by preventing designs from being destroyed.

1.2.2. Superhydrophobicity

Superhydrophobic fabrics have been available and are the recent concentration of studies in textile researches because of their numerous applications in the textile industry. An example is the ‘lotus effect’ which shows an excellent super anti-wetting with self-cleanable property of the surfaces of the leaves by which rain water rolls off smoothly than attaching to the surfaces.

These unique features have been accredited to the combination of the waxed covering that results in the lowering of the surface energy and the dual scale structure of the surface. The dermal tissue of the leaves develops projections which attribute to the lowering of the surface energy with single covering of the cells which have been closely packed. This covering which acts as skin: covers and protects the plants [12].

Other studies have also revealed that, superhydrophobic fibres that produce water contact angles which are higher than 150^o are extraordinary and exhibited by other surfaces from nature such as the ‘lotus leaf’ mentioned above. Also, the superhydrophobicity of a fibre or fabric arises because of the effects shown on the hierarchical micro and nano structures of surfaces and from low surface energy derived from the materials [13].

Superhydrophobic coatings and surfaces have been described as nanoscopic surfaces or layers, which repel water [14]. This happens when water droplets hit the coated surfaces and fully rebound in the shape of a column. Superhydrophobic surfaces have also been described as surfaces that repel water. In addition, the observed water contact angles have water droplets beyond 150^o while the droplets that produce the roll off angle is recorded less than 10^o to confirm that the fabric is truly superhydrophobic [15].

In addition, some researchers have come up with a new and mostly accepted meaning of a superhydrophobic surface as those surfaces on which the water or the advancing contact angle produces a least angle at 150° [16]. The water contact angle hysteresis has been classified as the most valuable and elegant factor considered in the absorption of liquid drops ranged from centimeter to micrometer scales. These are mostly understood intuitively by the observation of the water droplet resting on the horizontal surface [17] in figure 2.

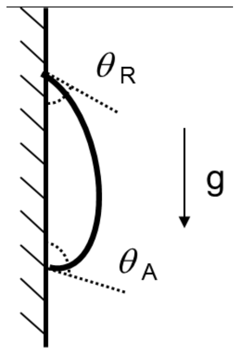


Figure 2. Water drop on a vertical surface, showing the critical advancing angle (θa) and the critical receding angle (θr) [17].

The contact angle hysteresis is like rain drop spotted on a window whereby the gravity draws the droplet in place. This makes the droplet to become asymmetric and static. The upper side of the droplet looks thin with a low contact angle. The 'bottom' or lower side thus becomes viscous and produces a high-water contact angle. The droplets move downwards in an asymmetric outline upon attaining some size [18]. The sliding or rolling off angle (contact angle hysteresis) refers to the lowest angle of sloped solid at which a water drop or a liquid drop rolls off the surface and not above 5-10^{o} [17].

In another research, a contact angle has been denoted by the symbol 'θ' and described as a quantity relating to a measurement of making a solid absorb liquid [19] and non-representationally as an angle produced by the liquid which has been developed resulting in producing a three-part borderline where the liquid, gas and solid intersects.

The equation below refers to as the 'Young equation' describes the fairness 'balance' at the three-part contact of the solid-liquid and gas. This 'balance' emphasizes on the interfacial tensions 'γ_{sv}, γ_{sl} and γ_{lv}' which form the 'equilibrium contact angle of wetting' referred to as 'Young contact angle θY'.

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta Y$$

The figure 3 explains the water contact angle at low values showing liquids spreaded on the uppermost layer with increased water contact angle values exhibiting a spreading not good but poor. It further shows that if the contact angle is less than 90^o, that means the surface has been wetted by the liquid where a ‘zero-contact’ angle denotes a ‘complete wetting’ of the surface. But a water contact angle greater than 90^o; the state is attributed to a hydrophobic state to a superhydrophobic state [18].

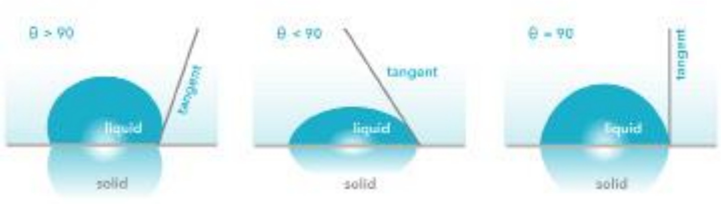


Figure 3. Contact angles at different levels on a surface [18].

In recent studies, two superhydrophobic states have been observed. These states are the ‘Wenzel’s state’ in figure 4 and the ‘Cassie’s state’ in figure 5. The ‘Wenzel’s state’ shows droplets of water that attach to the surface in a wet-contact mode, and as a result showed high contact angle hysteresis.

In reflection, water droplets that cannot slide on a surface are referred to as sliding angles that do not portray good measurements of the contact angles hysteresis that are high [20]. Figures 4 and 5 show the ‘Cassie’s state’ where the droplets of water could roll off easily; and this results in the low sticky force which gave way to the contact angle hysteresis to be recorded. The drop has a surface tension denoted by γ, a density denoted by ρ, a volume denoted by V, a height h, a contact diameter of 2a, and an apex radius of curvature denoted by b. The drop is suspended on cylindrical pillars and has often been referred to as the Cassie state [21].

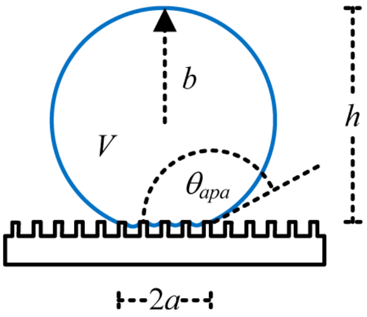


Figure 4. A small liquid depicting a superhydrophobic surface [20].

In figure 5, (a) shows the ‘Wenzel state’, (b) the ‘Cassie’s superhydrophobic state’, in (c) the ‘Lotus’ state which shows the special case of ‘Cassie’s superhydrophobic state’ has been shown, (d) shows the ‘transitional superhydrophobic state’ between ‘Wenzel and Cassie’s states’, and e) shows the ‘Gecko’ state of the ‘PS nanotube’ surface. The ‘air pockets’ also referred to as the ‘open state’ are shown in figure 4 with the grayed areas showing the ‘sealed air’.

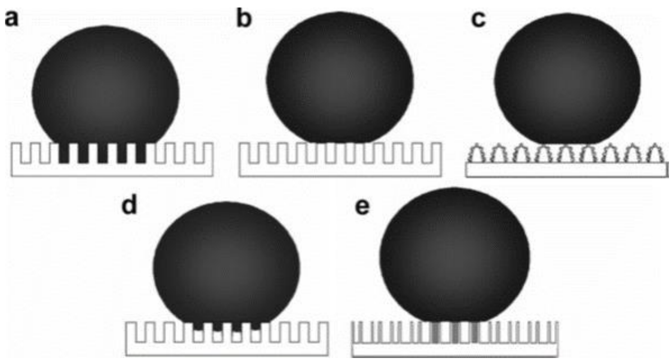


Figure 5. Superhydrophobic surfaces with different states [21].

In addition to the above studies on superhydrophobicity, other researchers have come out with the development of a superhydrophobic coloured cotton fabric by the 'sol-gel technique'. This development was done by combining 'silica nanoparticles', 'silane hydrophobes (alkyltrialkoxysilanes)', and 'silane cross-linkers (tetraethoxysilane (TEOS)' and 'teramethoxysilane - TMOS)' after dyeing fabrics with 'drimarene reactive red 5B' and 'drimarene reactive blue BR' dyes by the 'dip-dry-cure process' [22]. The research concluded that, observations confirmed a long-lasting hydrophobic property achieved on the treated dyed fabric with the 'non-fluorine sol-gel' process [22]. The silica nanoparticles used exhibited good fastness to colour and some effect on the shade. In addition to the above observations, the SEM images of the dyed coated fabric showed irregular surface behavior when compared to the uncoated dyed samples. The researcher also reported the increase of water repellency with silica concentration which was due to the deposition of silica nanoparticles in figure 6 (b). Also, the roughness of the surface in regards with the dyed coated samples have been reported to have provided the 'lotus effect', and that resisted the penetration of water and reduced the reflectance of light, to have an increased color strength values [3].

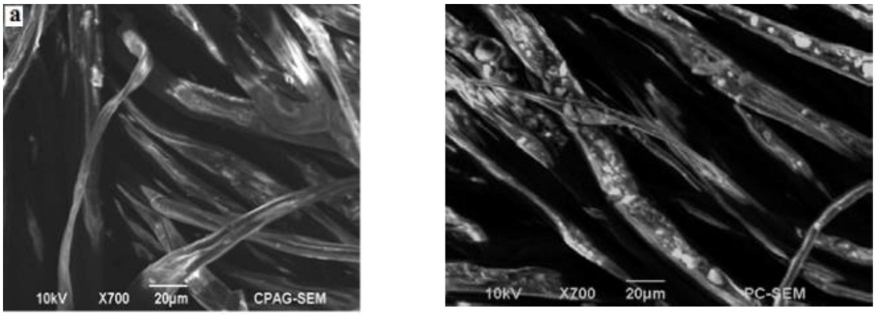


Figure 6. (a). Image of SEM before silica nanoparticles coating. (b) the SEM image after silica nanoparticles coating [22].

Another development of superhydrophobic dyed surfaces is the use of silica nanoparticles again to produce nano-roughened fabric surface. This was done with the aim of creating a superhydrophobic fabric dyed with a direct dye where the treated fabric was fast to washing [3].

1.2.3. Superhydrophobic development

Superhydrophobic 'nano-roughened surfaces' are produced by managing the substrate's topography with the use of varied methods. Some of these methods are; 'organic/inorganic hybrid method', 'electrochemical method' 'plasma method', 'phase separation method' and 'sol–gel method'. The coating method that employs the 'sol-gel' method enhances the features present in the fabric such as the colour of dyed fabrics used, the fastness to washing, and the rubbing fastness [23].

Other steps used in a superhydrophobic cotton fabric development are the production of cotton fabric with properties that resemble superhydrophobic inspired objects in nature either by a ‘one-step’ or ‘two-step’ reaction [24]. The varied methods used are outlined in table 1 for development on cellulosic-based surfaces [1]

Table 1. Some common methods used for superhydrphobic developments on cotton surfaces and cellulosic-based substrates [1].

Methods	Roughness Formation	Time-Scale and Requirement [a]	Properties
Dip-coating	Nanoparticle coating	Slow	Mechanical and environmental stability
Wet chemical etching	Growth of nano-structures by etching	Rapid/slow	Excellent resistance to washing, abrasion
Chemical bath disposition	Nanoparticle film deposition	Slow and temperature requirement	Moderate durability
Electrophoretic deposition	Nanoparticle coating	Rapid and conductive substrate requirement	Chemical stability, highly transparent
Electrospinning	Nanofibers by electrospinning	Slow and solvent requirement	Porous membrane
Spray-coating methods	Micro/nanostructures by spraying	Rapid and scalable under ambient conditions	Moderate stability, easy reparability
Chemical vapor deposition	Growth of nano structures by polymerization	Slow and need heating	Separation of oils or organic contaminates from water
Plasma etching process	Growth of nanostructures by etching	Moderate and require specific equipment	Self-cleaning

To add to the above approaches, cotton fabrics with superhydrophobicity have been developed by coating of fabrics using the ‘sol–gel’ of ‘TiO_2’ and surface hydrophobic coating [25]. However, micro with nanoscale hierarchical structures [4] regarding the results obtained are good proves essential in coming out with a superhydrophobic and self-cleanable substrate [4] that has great potential for various scientific and industrial applications.

1.2.4. Superhydrophobic development using zirconia particles

With the use of zirconium nanoparticles for producing a superhydrophobic surface, a ‘fluorinated silyl-functionalized’ zirconia with a high permanent sol-gel derived was experimented with an immersion method [26]. Results from the researcher indicated that, the fabrication did not deteriorate the original flexibility of the fabric but rather possessed an excellent long-lasting superhydrophobic and superoleophilicity property with a good water contact angle at 163^{o} and a contact angle hysteresis at 3.5^{o}. In addition, the studies indicated that, the ‘fluorinated silyl-functionalized’ zirconia coated fabric rather produced a very good sustainable and durable superhydrophobic fabric than particles with silica and other hydrophobization coatings which are not suitable for everyday technical usages [26].

In figure 7 the diagrammatic representation of the treated fabric for the principle of the reaction during the formation of the of the treated cotton fabric. In figure 8, images of the treated and untreated fabrics have been shown with (a) indicating the dyed-liquid on the untreated and treated surfaces, (b) showing the water drops on both the untreated and coated cotton surfaces. The (c) shows the ‘graphene oxide powder’ on the coated surface to explain in detail the self-cleaning property test. And in figure 8c, the drops of water that mixed up with the graphene powder used have been shown. [26].

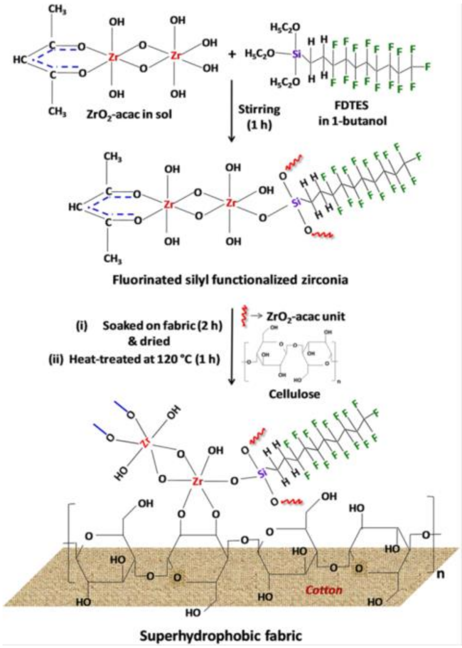


Figure 7. A chemical diagrammatic view of the treated fabric [26].

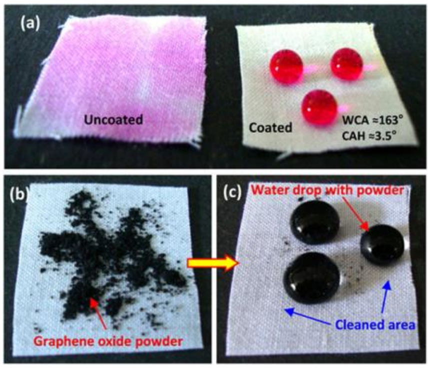


Figure 8. Images of the untreated and treated fabric [26].

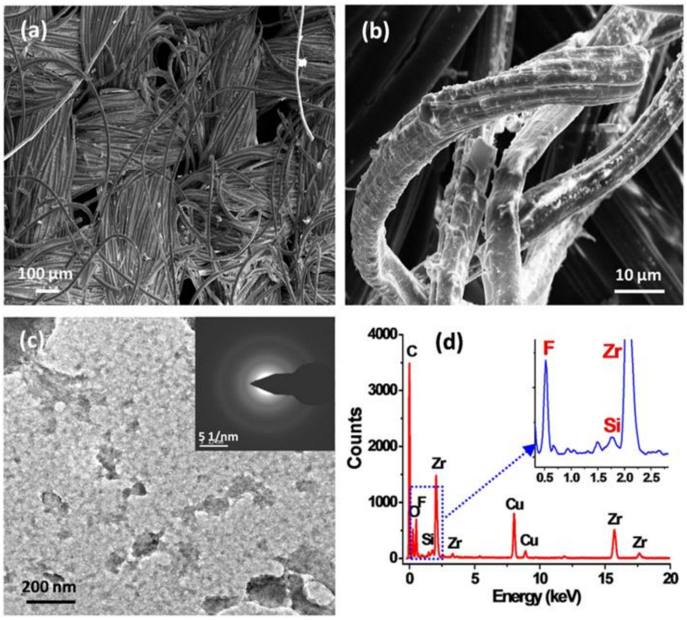


Figure 9. The FESEM and TEM analysis of the treated fabric exposed tio heat-treatment at 120^{o}C [26].

Finally, a simple inexpensive with durable superhydrophobic coating have also been developed on the surfaces of the cotton fabric using ‘no fluorine hydrophobic reagents’ which possessed photocatalytic properties. This was done by combining zirconia particles and ‘AgBr modification’ [2]. The mixed-composed mixture used in figures 10-12 confirmed the coated fabrics displayed superhydrophobicity with superoleophilic abilities of oil contact angle of 0^{o}, water contact angle at 153^{o} and water sliding angle at 7^{o} in figure 10 [2].

Figure 10. A diagrammatic skectch of developing the treated fabric by the dip coating method [2].

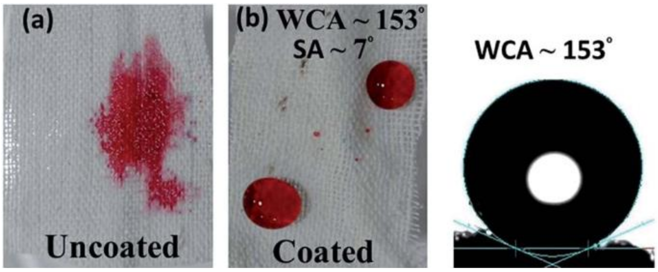


Figure 11. Optical images of dyed (phenosafranim) water drops on untreated and fabric in (a) and treated fabric in (b) [2].

Scanning electron microscopy images from the studies revealed that, the surfaces of the coated fabrics had rougher surfaces than the coated original fabric and this has been assigned primarily to the homogeneous accumulation and dissemination of the particles used for coating the surface that lied in the spaces of the fibres of the treated cellulose [26].

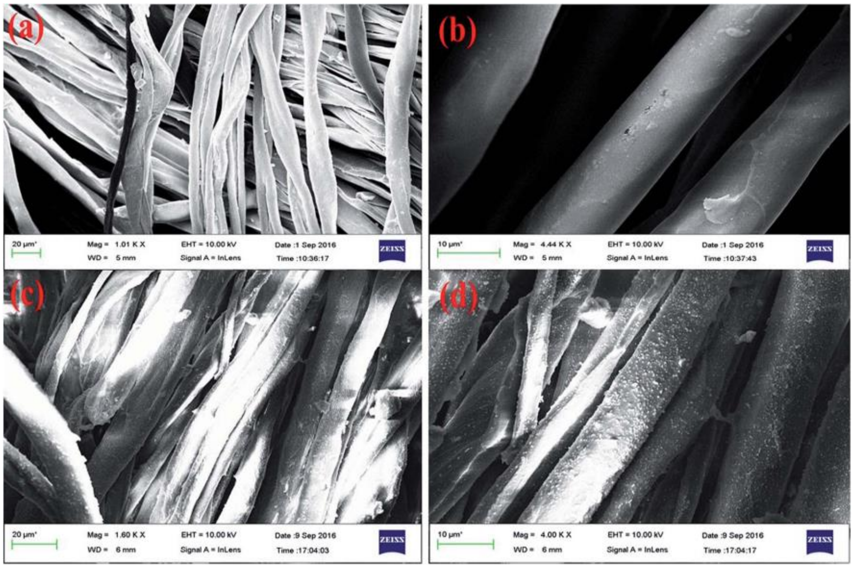


Figure 12. Images of scanning electron microscopy of the untreated cotton [2].

Experimental

2.1. Materials

A digital-printed cotton fabric was printed with UJET MC3 Premium by Yuhan Kimberly on a pre-treated cotton fabric. The digital-printed samples were cut 15cm X 15cm and cleaned with Ethyl alcohol anhydrous 99.9% - (C_2H_50H) purchased from Daejung KOSDAG listed Company Korea, and deionised water before subjecting to treatment. Methyl alcohol - (CH_3 OH) also obtained from Daejung KOSDAG listed Company, Korea; used as a dissolving agent for dodecyltriethoxysilane ($C_{15}H_{34}O_3Si$) as silane hydrophobes obtained from Sigma-Aldrich, was used for synthesizing the sol to lower the surface energy.

For hierarchical nano roughness, zirconium (IV) propoxide solution 70 wt. % in 1-propanol (Zr ($OCH_2CH_2CH_3)_4$) from Sigma-Aldrich, product of U.S.A. was dissolved in 1-Butanol (CH_3 $(CH_2)_2CH_2OH$) from JUNSEI Chemical Co., Ltd. Lot No. 5E5810 with acetyl acetone ($CH_3COCH_2COCH_3$) from JUNSEI Chemical Co., Ltd. Lot No. 2017D2026 used as a chelating agent to stabilize the zirconium nanoparticle (Zr ($OCH_2CH_2CH_3)_4$).

2.2. Digital Printing and Superhydrophobic Treatment

2.2.1. Digital-printing and fixation of pigment

The original cotton fabric was pre-treated by dissolving sodium alginate in 50 grams of deionized water -0.95 dm^3, sodium bicarbonate of 8 grams, and urea -10 grams [27-29]. The weight of the paste was 200 grams of deionized water [27-29] which was mixed thoroughly. The paste used to treat the original fabric before printing was applied on the original cotton fabric by the use of a ‘padding machine’. The pressure used was even and at 2.6 kg/m^2 with a ‘padding speed’ at 2.5rpm. This continued until the original fabric being treated reached a percentage of 80% of ‘pick-up’ of the solution mixed after which the coated pre-treated cotton fabric was dried at 80o in an oven. Before digital printing, the pre-treated cotton fabric underwent a conditioning treatment [27-29].

Digital printing was done using the digital printing machine- UJET MC3 Premium by Yuhan Kimberly with Reactive LT CMYK digital textiles printing pigment in figure 8a with additional pigments used which were light magenta, orange, gray and blue. The printing resolution was set at 300dpi. After printing, the digital-printed fabric was steamed twice to wash-off excess printing pigments and to fix the printing pigment into the fabric structure at 95 ^oC for 40 minutes. Steamed digital-printed fabrics could dry under room temperature overnight and dried digital-printed fabric shown in figure 14. Figure 15 shows the overall process of treating the original cotton and finally printing the digital-printed fabric.

Figure 13. Digital Textile Printing of pre-treated fabric.

Figure 14. Steamed digital-printed fabric.

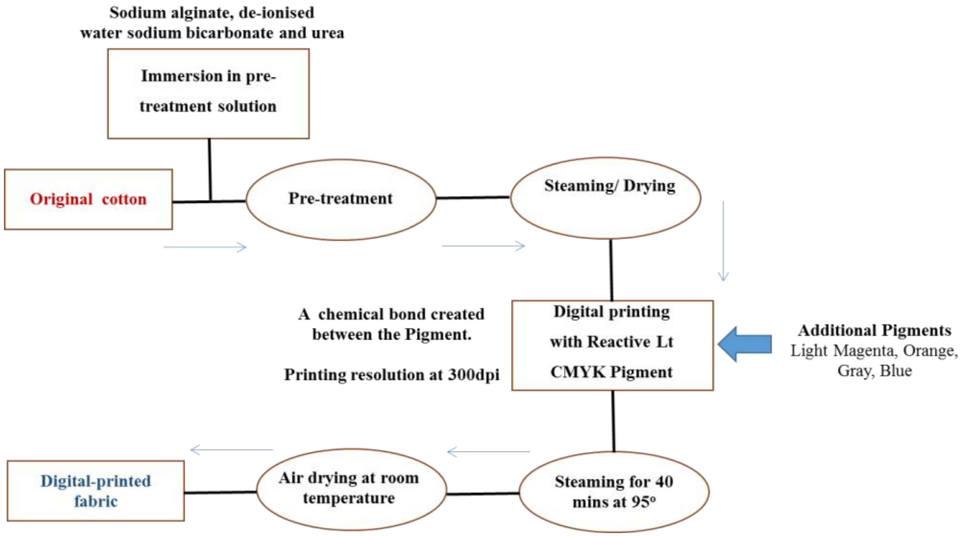


Figure 15. Digital Textile Printing of original cotton fabric from the pre-treatment stage to the final digital-printed fabric.

2.2.2. Preparation of cotton fabric

Prior to superhydrophobic treatment, the original cotton fabric and digital-printed fabric samples were treated with deionized water and Ethyl alcohol anhydrous 99.9% - (C_2H_5OH) [29]. Fabrics were dried under room temperature and 3 digital-printed fabric samples were cured at 100^{o}C, 120^{o}C and at 140^{o}C without the use of water due to the high temperature required in fixing reactive dyes into the fibre structure of cotton fabric during printing; whereby dye fixation was done by heat-treatments based on the following techniques [30]:

(1) Steaming by saturated vapour (100^{o}C).

(2) High temperature steaming by super-heated vapour at temperature conditions from 120-150^{o}.

(3) Dry eating by hot air which is a thermofix process at temperatures from 150-200^{o}.

Sample coding

Table 2 shows the sample codes used in this study with the original fabric sample names.

Table 2. Samples used and their respective sample codes.

Samples of fabrics used	Sample codes
Original fabric	**O**
Digital-printed fabric	**P**
Digital-printed cured fabric	**PC**
Digital-printed and superhydrophobic treated fabric	**PCS**
Original superhydrophobic treated fabric	**S**
Superhydrophobic heat-treated samples after coating durability test	**SH, PCSH**

2.2.3. Fabrication of superhydrophobic digital-printed fabric

To lower the surface energy, silane sol was first prepared by dissolving 20ml dodecyltriethoxysilane ($C_{15}H_{3}4O_{3}Si$) in 10ml of methyl alcohol -(CH_{3} OH) in the ratio 2:1 with a dropwise addition of 10ml deionized water in table 3 and stirred magnetically for 1 hour at 400 rpm. Dodecyltriethoxysilane ($C_{15}H_{34}O_3Si$) was used to increase the bonding mechanism with zirconium as silane coupling agents improve the resin zirconia bonding significantly [31]. The percentage volumes of each material used in synthesizing the sol for the superhydrophobic treatment of the digital-printed fabric have been shown in table 4.

To add to the above, dodecyltriethoxysilane ($C_{15}H_{34}O_3Si$) was used because the more the ‘hydroxyl groups’ on the surfaces of the ‘silane-coated’ zirconium, the higher the level of bonding in-between the ‘silane primer’ and the zirconium-coated surface where a lot of energy would be needed to interrupt the ‘interfacial’ layer [32].

To produce a superhydrophobic digital-printed fabric with hierarchical roughness, zirconium sol was synthesized according to previous report [26] and modified to suit the current study without the use of fluorinated materials because; zirconium exhibited a very good mechanical strength which possesses a high relationship with energy that does not dissociate at ~ 753 KJ mole-1 [33] and as well; a strong covalent character of which it has been noted for [34]. Zirconium has also been well known for its stability thermally [35] as well as the ability to withstand strong alkali and acid when compared with other particles also of the ceramic origin [36].

A 10ml of zirconium nanoparticle (Zr ($OCH_2CH_2CH_3)_4$) was dissolved in

10ml 1-Butanol ($CH_3(CH_2)_2CH_2OH$) in the ratio 1:1. Stirring was done for 1 hour at 400 rpm magnetically after which 2ml acetyl acetone ($CH_3COCH_2COCH_3$) was added by dropwise addition as a chelating agent to remove toxins and stabilize the zirconium nanoparticle ($Zr(OCH_2CH_2CH_3)_4$). The synthesized sol was stirred again magnetically for one hour all under cold temperature.

Table 3. Concentration of materials for the fabrication of the superhydrophobic digital-printed fabric.

Materials	Concentration (ml)
Methyl alcohol	10
Dodecyltriethoxysilane (Silane Hydrophobes)	20
Deionized Water	10
1-Butanol	10
Zirconium (IV) propoxide solution 70 wt. % in 1-propanol	10
Acetyl Acetone	2

Table 4. Concentration of materials for the fabrication of the superhydrophobic digital-printed fabric.

Materials	Vol %
Methyl alcohol	10/62 = 0.16)
Dodecyltriethoxysilane (Silane Hydrophobes)	20/ 62 = 0.32
Deionized Water	10/62 = 0.16
1-Butanol	10/62 = 0.16
Zirconium (IV) propoxide solution 70 wt. % in 1-propanol	10/62 =0.16
Acetyl Acetone	2/62 = 0.03

The silane sol was added to the zirconium sol and stirred magnetically for 1 hour at 400rpm. Samples were dipped into the sols for one hour and heat-treated under different temperature degrees to ascertain the temperature condition suitable for superhydrophobic development on digital-printed surfaces as reactive pigments require a set temperature condition to adhere into the fabric structure [30]. In figure 16, the schematic structure has been represented showing the preparation for fabrication. Figure 17 shows the schematic surface structure for the fabrication of superhydrophobic digital-printed fabric and in figure 18, the overall treatment procedure for the fabrication of the superhydrophobic digital-printed fabric has been outlined.

After washing off excess nanoparticles, the samples were then re-coded as sample **S** being the original fabric O before superhydrophobic treatment; heat treated at 120^{o}C after superhydrophobic treatment, sample **PS-** the superhydrophobic treated digital printed fabric P heat treated at 120 ^{o}C, sample **PCS/100-** the treated superhydrophobic digital-printed fabric cured at 100 ^{o}C; sample PC/100 before superhydrophobic treatment which was heat-treated after superhydrophobic treatment at 100 ^{o}C, sample **PCS/120-** the treated superhydrophobic digital-printed fabric cured at 120^{o}C before superhydrophobic treatment- PC/120 which was heat-treated after superhydrophobic treatment at 120 ^{o}C and sample **PCS/140 -** the treated superhydrophobic digital-printed fabric cured at 140^{o}C before superhydrophobic treatment- PC/140 heat-treated after superhydrophobic treatment at 140°C. All heat treatment lasted for one hour for all samples.

a

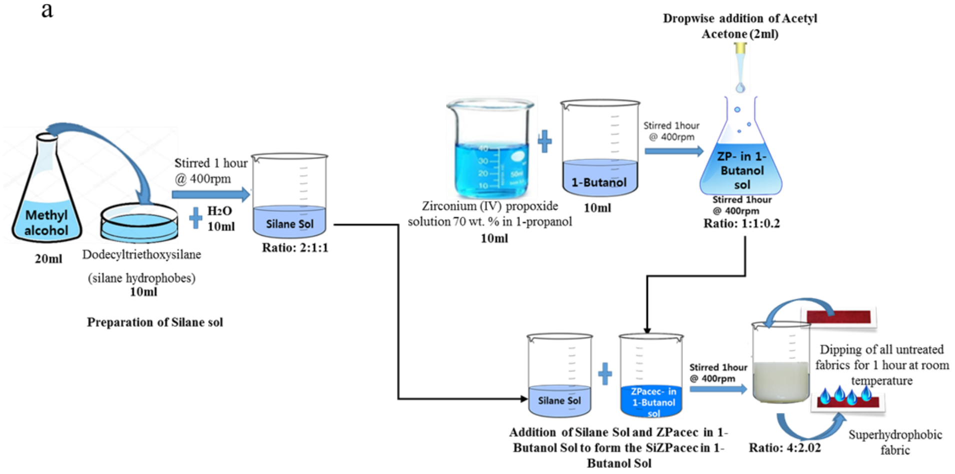


Figure 16. A diagrammatic representation of the preparation of sol and fabrication of superhydrophobic digital-printed fabric.

b

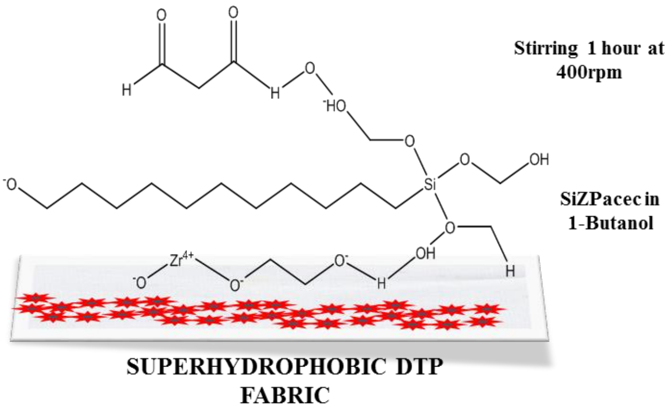


Figure 17. A diagrammatic surface structure for the chemical reaction on the surface of the treated digital-printed fabric.

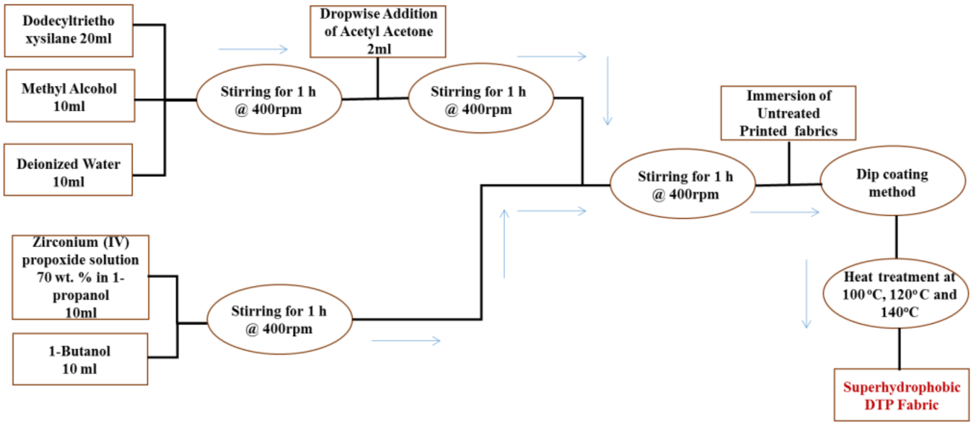


Figure 18. Overall treatment procedure for the treatment of the digital-printed fabric.

2.3. Characterization

The surface morphology of untreated fabric samples O, P, PC/100, PC/120, PC/140 and superhydrophobic treated samples S, PS, PCS/100, PCS/120, PCS/140 was monitored using the ESC 7900 scanning electron microcopy. Water contact angle and water shedding angle measurements were conducted with the water contact angle goniometer ‘Theta lite optical tensionmeter, KSV Instruments, Finland’ and the shedding angle adjustment by using the ‘cradle (Attention theta lite)’ on treated and untreated samples. Colour difference was tested with the colour spectrophotometer ELECOM U2H-M4BGT S/N003090. An air permeability test was done with the Testing Instruments for Quality Control. Zurich, Switzerland TEXTESTAG (FX 3300)

2.3.1. Evaluation of surface morphology

The fundamental composition and surface morphology of developed digital-printed cotton fabric samples and undeveloped digital-printed cotton fabric samples was examined by the scanning electron microcopy ESC 7900. Before the examination of the surface morphology, a sputtering coater was used by depositing a thin layer of gold film to cover all samples surfaces to aid in increasing the conductivity of the structures during the main experiment.

2.3.2. Evaluation of water contact angle and shedding angle

The water contact angle measurement and shedding angle measurement tests have been done using the contact angle goniometer. Both treated and untreated sample surfaces were measured and compared by using a sessile water drop method with water droplets of distilled water up to 10-15µl on all fabric samples without any set temperature conditions. The results of the water contact angles and shedding angles were measured on two different samples at five separate points. The mean values of the contact angles were recorded. The photographs of the water droplets on the surfaces of the fabric samples were captured with the use of a digital camera between 10-20 seconds. This was done without changing the temperature and the air flow of the testing environment.

The measurement of the shedding angle was also done by dropping the liquids on the surfaces of the untreated and treated fabric samples which was very difficult to record due to the stickiness of the surfaces of the treated digital-printed fabrics and then hydrophilic nature of then untreated fabric samples. This was based [14], on the roll-off angles of the various samples to be proven as a superhydrophobic substrate.

2.3.3. Evaluation of colour difference

The colour difference of the steamed digital-printed fabric, digital-printed fabric washed with ethyl alcohol and deionized water; zirconium treated digital-printed cotton fabric and treated digital-printed cotton fabric that had undergone five washing cycles were tested. The same colour points were cut out and measured for the colour difference since the digital-printed fabric sample used in this study was a patterned digital-printed fabric. The samples were measured with the colour spectrophotometer ELECOM U2H-M4BGT S/N003090 to find out the effect of treatment on colour based on the colour difference at observer 10^{o} (Primary: D65). Results of the L* values at D65 were recorded since the colour brightness results were used to assess the colour difference.

2.3.4. Evaluation of air permeability

An air permeability test was performed on the various samples to evaluate air passage of the treated surfaces which could affect the air pores of the treated fabric samples. The untreated and treated fabric samples were tested with the Testing Instruments for Quality Control Zurich, Switzerland TEXTESTAG (FX 3300).

2.3.5. Various liquids' repellency tests

The repellency of other liquids was tested with various liquids by comparing all fabric samples- both the treated and the untreated. This was executed by dropping droplets of various liquids on the sample surfaces. The various liquids used to test the surface repellence of the treated fabrics were coloured water, cocoa drink, black tea, cranberry juice and coffee. These liquids were selected to evaluate the surface repellency of the treated surface to ascertain the repellency of the treated surface to other liquids apart from water.

2.3.6. Evaluation of coating durability

All superhydrophobic treated fabrics underwent five washing cycles at $40^{o}C$ for 39 mins in a commercial washing machine. This was to compare the durability of the superhydrophobic digital-printed fabrics with the superhydrophobic original cotton fabric for better assessment of the printing pigment based on the water contact angles, and the colour difference.

After the first, third and fifth laundry cycles before and after healing treatment water contact angle measurements were taken. During the healing treatment, fabric samples were subjected to heat-treatment for 5 minutes. Measurement of the water contact angles was also to find out if all treated fabric samples maintained their superhydrophobicity after the five laundry cycles and could possess self-healing properties after being washed five times. After each washing cycle, the state of firmness and strength of treatment on the samples was determined by measuring the water contact angles.

2.3.7. Self-cleaning property of fabricated digital-printed fabrics

The self-cleaning ability test was conducted with silicon carbide to find out if treated samples had the ability to self-clean without any external force on the surfaces. This was recorded with the use of a digital camera to find out the self-cleaning performance of all samples used in the experiment.

Results and Discussion

3.1. Surface morphology of treated and untreated fabrics

Surface morphology results confirmed the original cotton fabric in figure 19, (a) with a smooth surface structure of the fibre with fine terraces visible features on its fibre cuticle at a low magnification, while (b) shows a low magnification of the superhydrophobic developed original fabric - S with roughened surface structures indicating the deposition of the nanoparticles employed in this study on the surface of the fibre thereby altering the fibre structure and surface. The (c) shows the high magnification of (b).

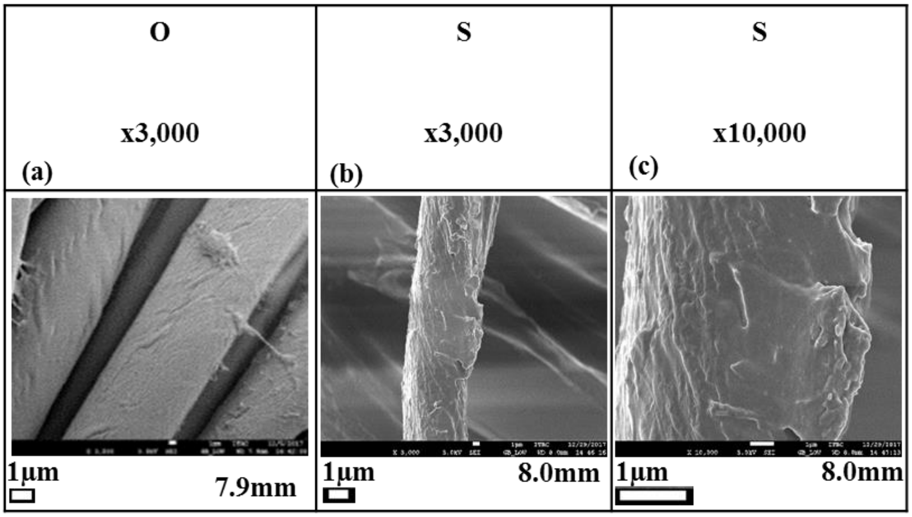


Figure 19. The surface morphology of the original cotton fabric -O in (a), S in (b) at a low magnification and S at a higher magnification in (c).

The surface morphology of the digital-printed fabric -P in figure 20 where (a) shows a very slight rough surfaces on the cotton subsrate due to the deposition of the printing pigment. In (b), the treated digital-printed fabric -

PS shown at a low magnification of after heat-treatment at 120°C had more roughened surfaces owing to the changing of the fibre surface and structure showing deposition of the nanoparticles used thereby recording the highest at 162° due to the change in morphology of the coated surface. The higher magnification in (c) clearly demonstrated the structure after treatment, by becoming rougher and uneven.

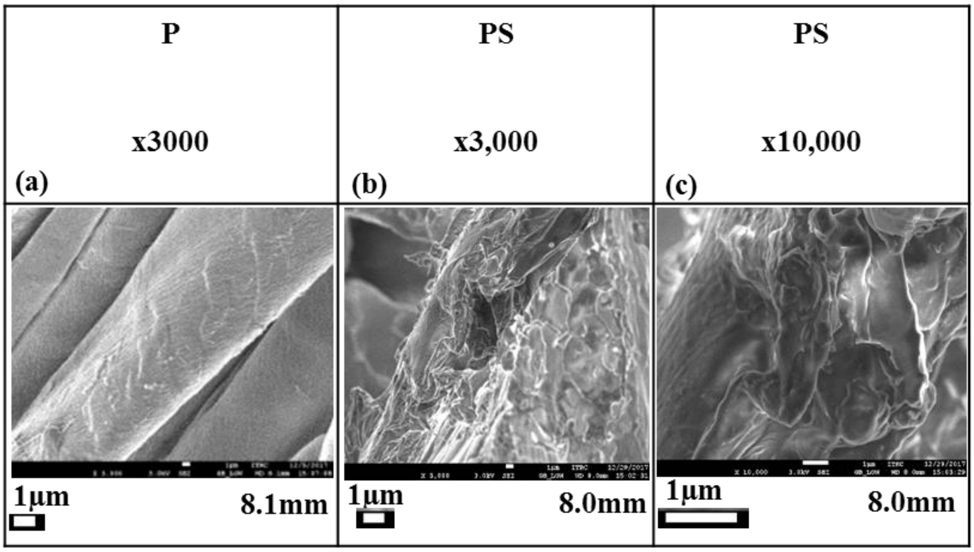


Figure 20. The surface morphology of the digital-printed fabric -P in (a), PS in (b) at a low magnification and PS at a higher magnification in (c).

The digital-printed fabric cured at 100° before superhydrophobic treatment-PC/100 in figure 21, (a) had a smooth surface with slight rough patches while (b) shows the superhydrophobic digital-printed fabric -PCS/100 with some kind of rough surface and a meandering glossy effect which could be due to the the curing before superhydrophobic treatment in a low magnification. The higher magnification of (b) is shown in (c).

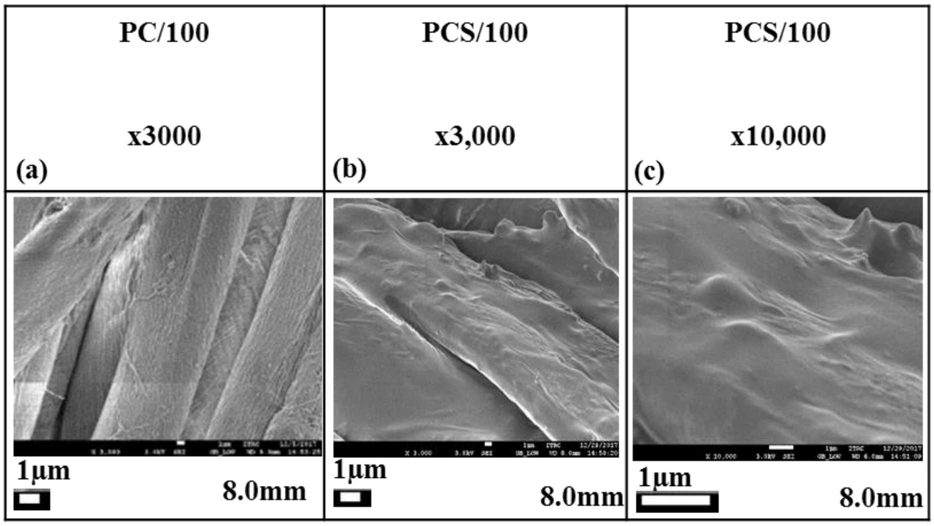


Figure 21. The surface morphology of the digital-printed fabric PC/100 in (a), PCS/100 in (b) at a low magnification and PCS/100 at a higher magnification in (c).

The digital-printed fabric cured at 120^{o} before superhydrophobic treatment - PC/120 in figure 22, (a) also shows a smooth surface with slight rough patches which could be due to the printing pigment and the temperature at which the digital-printed fabric was cured before superhydrophobic treatment. The (b) shows the superhydrophobic digital-printed fabric - PCS/120 with more roughened surface than (a) and some glossy effects in a low magnification. The higher magnification of (b) is shown in (c).

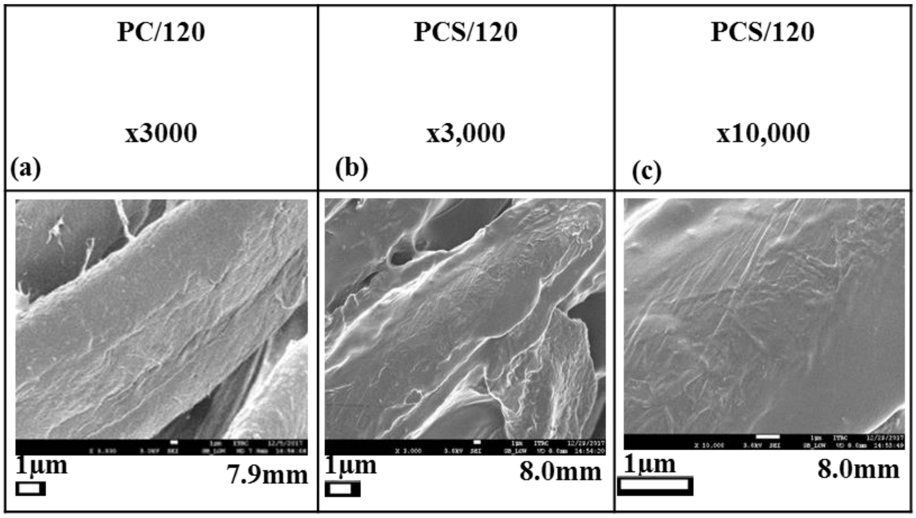


Figure 22. The surface morphology of the digital-printed fabric PC/120 in (a), PCS/120 in (b) at a low magnification and PCS/120 at a higher magnification in (c).

The digital-printed fabric cured at 140^{o} before superhydrophobic treatment -PC/140 in figure 23 where (a) shows a smooth surface of the untreated digital-printed fibre structure while (b) shows the superhydrophobic digital-printed fabric -PCS/140 with rougher surface and less glossy effect than in figures 12 and 13 which could also be due to the the curing before superhydrophobic treatment and deposition of the superhydrophobic particles in a low magnification. The higher magnification of (b) is shown in (c).

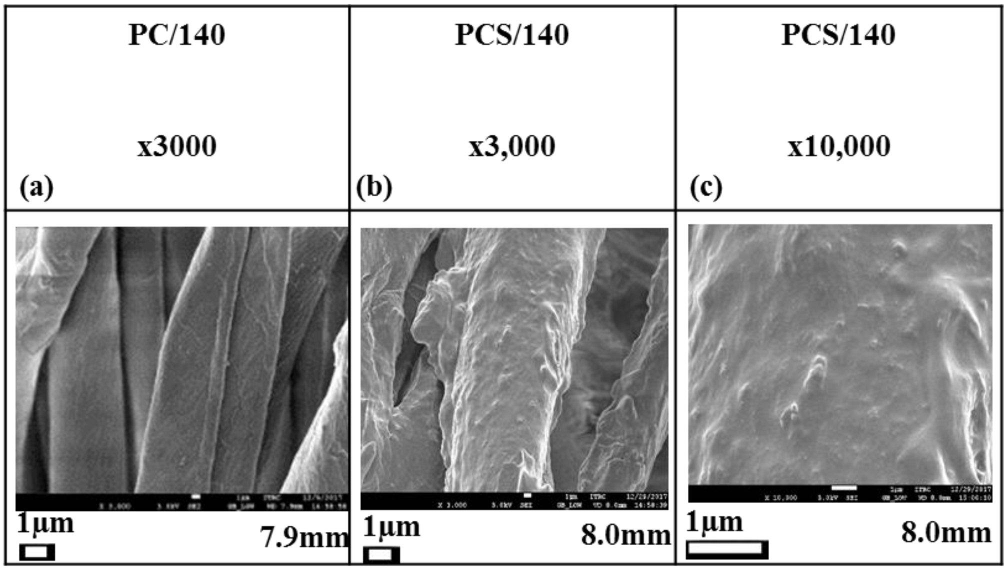


Figure 23. The surface morphology of the digital-printed fabric PC/140 in (a), PCS/140 in (b) at a low magnification and PCS/140 at a higher magnification in (c).

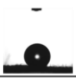
3.2. Water contact angle and shedding angle

Based on the ‘ASTM D7334-08(2013)-Standard Practice for Surface Wettability of Coatings, Substrates and Pigments’, the results of the water contact angle confirmed complete wetting for all fabric samples. The wettability of the original cotton sample after contact angle measurements exhibited the typical cotton fabric, due to the wetting group called the ‘hydrophillic groups’ in the fabric structure made up of cellulose that absorbed all the water.

After the steaming process, the pre-tretatmnent elements were lost in the untreated digital-printed fabric by rendering it hydrophillic thereby losing the hydrophobic property.

Further results of the water contact angle confirmed the digital-printed fabric - PS with the highest water contact angle at 162^{o} whiles PCS/100 recorded the lowest water contact angle at 150^{o}. PCS/120 recorded an average of water contact angle at 153^{o}. The PCS/140 recorded an average water contact angle at 154^{o} in table 5.

Table 5. Water contact angle and shedding angle of untreated samples and treated samples with the contact angle images of superhydrophobic treated samples.

	UNTREATED SAMPLES					SUPEHYDROPHOBIC TREATED SAMPLES				
	O	**P**	**PC/100**	**PC/120**	**PC/140**	**S**	**PS**	**PCS/100**	**PCS/120**	**PCS/140**
Water Contact Angle (°)	**0** (Complete wetting in less than 5 sec)	**0** (Complete wetting in less than 5 sec)	**0** (Complete wetting in less than 5 sec)	**0** (Complete wetting in less than 5 sec)	**0** (Complete wetting in less than 5 sec)	**161** 	**162** 	**150** 	**153** 	**154** 
Shedding Angle (°)						**20**	**14**	**19**	**20**	**30**

The results concluded that, printing before superhydrophobic treatment had no effect on the superhydrophobicity but rather the temperature condition of heat treatment. Curing before superhydrophobic treatment at various temperature degrees also confirmed the temperature conditions interfered with the pigment by exposure to excessive heat after steaming twice at 95^{o} for 40 minutes by breaking down the chemical structures of the cured digital-printed fabrics before treatment.

On the other hand, the untreated samples had complete wetting based on the water contact angle results and water could not roll off the surfaces. Therefore, it was impossible when taking measurements of the shedding angle of the untreated samples.

The shedding angles of the superhydrophobic treated samples recorded were higher than 10^{o} due to the sticky surface of the treated fabrics. In figure 24, the water contact angle and shedding angle results of the treated fabric samples have been shown in detail.

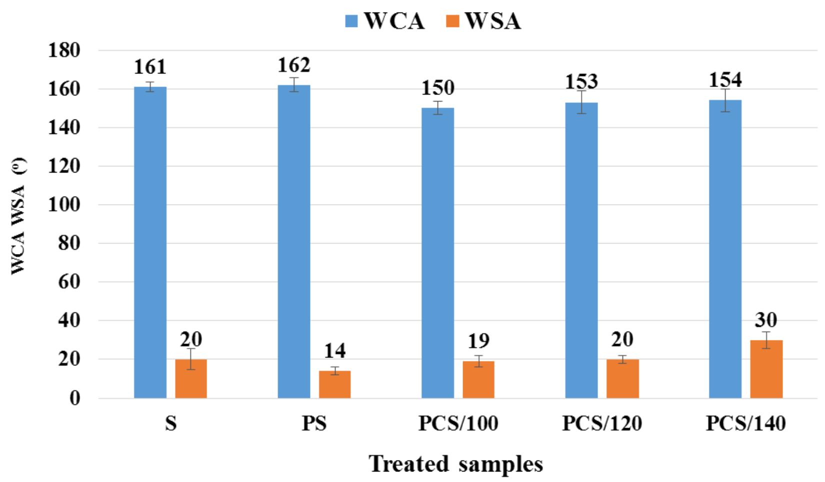


Figure 24. Graph showing the water contact angle and water shedding angle of treated fabric samples.

3.3. Repellency

Observation of the surface repellency to water by visual examination with various liquids (coloured water, cocoa drink, black tea cranberry juice and coffee) dropped on the surfaces showed that, the original cotton sample -O absorbed completely in less than 3 seconds. Also, the untreated digital-printed cotton sample -P absorbed all liquids completely.

The superhydrophobic treated digital-printed fabric -PS showed much repellency when the various liquids were dropped on the surface to other liquids apart from water which could be because of the air layer trapped on the digital-printed cotton surface. Likewise the superhydrophobic treated original cotton fabric -S did not absorb any of the afore-mentioned liquids compared to the original cotton fabric which is a phenomenon that proving the ‘Cassie-Baxter state’ of the finished treated fabric samples [1] in figure 25.

Figure 25. Images of various liquid droplets on the surfaces of untreated fabrics, and treated fabrics with coloured water, cocoa drink, black tea, cranberry juice and coffee.

3.4. Durabilty of coating before heat treatment

A very significant factor for functionality of the prepared fabric is the durability test by subjecting treated fabric samples to a number of washing cycles based on the fact that the superhydrophobic digital-printed cotton fabrics would be in the future subjected to washing in the environment. The water contact angle of treated samples have been shown in fifure 26 before heat treatment. Water contact angle results before washed samples were subjected to heat treatment confirmed the superhydrophic digital-printed fabric -PS recorded the highest water contact angle at 159 ^{o} compared to the water contact angle result before first washing cycle at 162^{o} in figure 27. The superhydrophic digital-printed fabric -PCS/100 increased in water contact angle before heat treatment from 150 ^{o} to 153^{o} which could be due to uneven heat-treatment before evaluation of the coating durabilty. Only the superhydrophic digital-printed fabric PCS/140 recorded the lowest water contact angle at 122^{o} after all washing cycles before heat treatment.

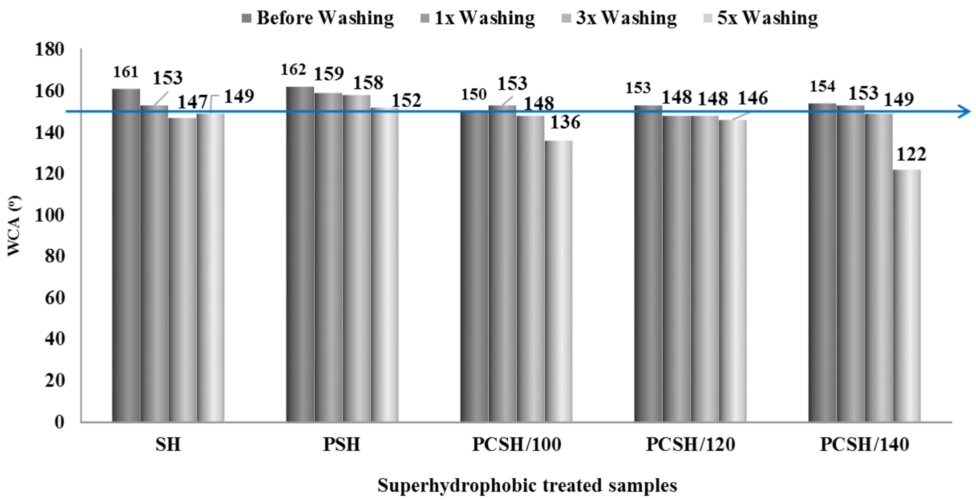


Figure 26. Water contact angles after all washing cycles before heat treatment in comparism with water contact angles before washing cycles.

3.5. Durabilty of coating after heat treatment

After heat treatment for 5 minutes at various temperature conditions, the superhydrophic digital-printed fabric -PS recorded the highest water contact angle at 156^{o} after all washing cycles compared to the water contact angle at

162^o before coating evaluation, and at 152^o before heat treatment after all washing cycles. The superhydrophobic digital-printed fabric -PCS/120 recorded a water contact angle slightly below 150^o at 148^o making it hydrophobic after all washing cycles which could be due to excessive exposure to heat since the superhydrophic digital-printed fabric -PCS/120 was cured before superhydrophobic treatment at 120^o. This could also break down the fibre structure of the treated superhydrophic digital-printed fabric -PCS/120 based on the water contact angle results in figure 18.

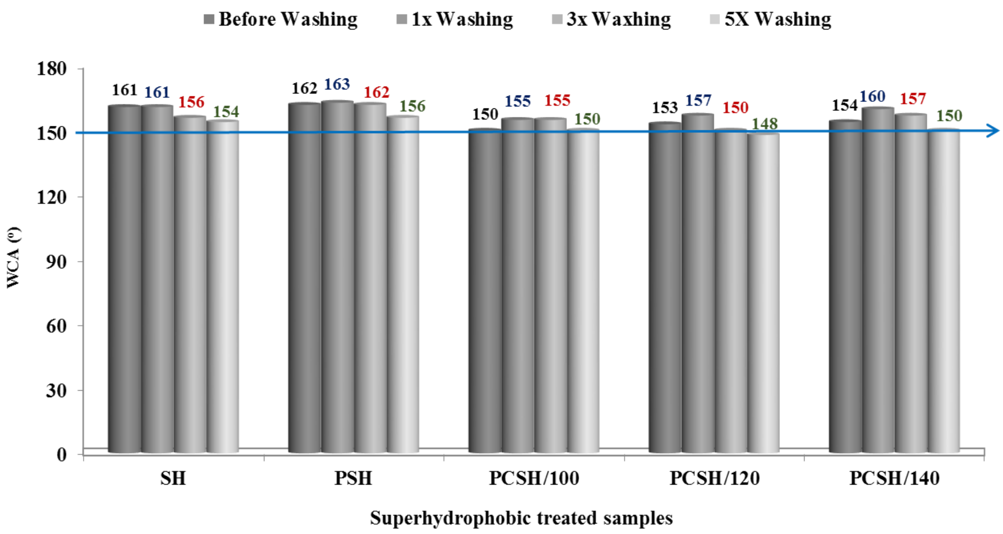


Figure 27. Water contact angles after heat treatment in comparism with water contact angles before washing cycles.

3.6. Effect of treatment on colour

The outcome values from the spectrophotometer and images for the visual examination have been shown in table 6 where the digital-printed fabric had a decrease in the light-shaded colour tested after cleansing with deionized water and ethanol based on the results from the colour spectrophotometer with L* value of 84.4 at D65 After superhydrophobic treatment, the light-shaded colour decreased and became shady with the lowest result at L* value of 63.4 at D65 which could be due to the deposition of the superhydrophobic particles on the surface of the digital-printed fabric because; the results recorded after five washing cycles rather increased to L* value of 76.6. at D65.

Visually, the difference could have amounted to the removal of some of the superhydrophobic particles deposited after all washing cycles with the little effect on the shade. The outcome values based on the results of the colour spectrophotometer also shows the difference in the brihtness in figure 28.

Table 6. Colour difference of effect of treatment on colour with images of digital-printed fabric samples -(after steaming, after cleaning with deionized water and ethanol, after superhydrophobic treatment and after 5 washing cycles).

Steamed digital-printed fabric	**After cleaning with deionized water and ethanol**	**After superhydrophobic treatment**	**After 5 washing cycles**
			
L* (D65) = 85.6	**L* (D65) = 84.4**	**L* (D65) = 63.4**	**L* (D65) = 76.6**

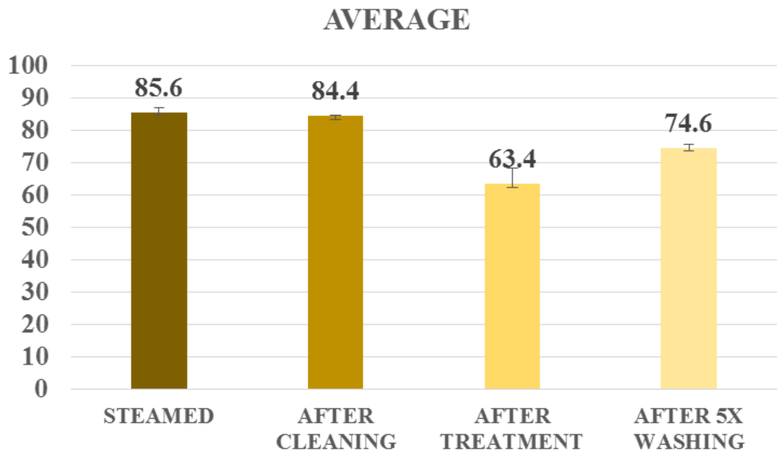


Figure 28. Graph showing the effect of treatment on colour of digital-printed samples -(after steaming, after cleaning with deionized water and ethanol, after treatment and after 5 washing cycles).

3.7. Air permeability

Superhydrophobic digital-printed fabric cured at 100^o - PCS/100 recorded the highest air permeability at 52.4 (cm3/cm2/s) and proved more breathable than the other samples. The other superhydrophobic treated fabric fabric samples because of their ‘high-density’ nature of how the packed the yarns became in the various stuctures produced rather a low flow of air at an average of 32.3 ($cm^3/cm^2/s$) in figure 29.

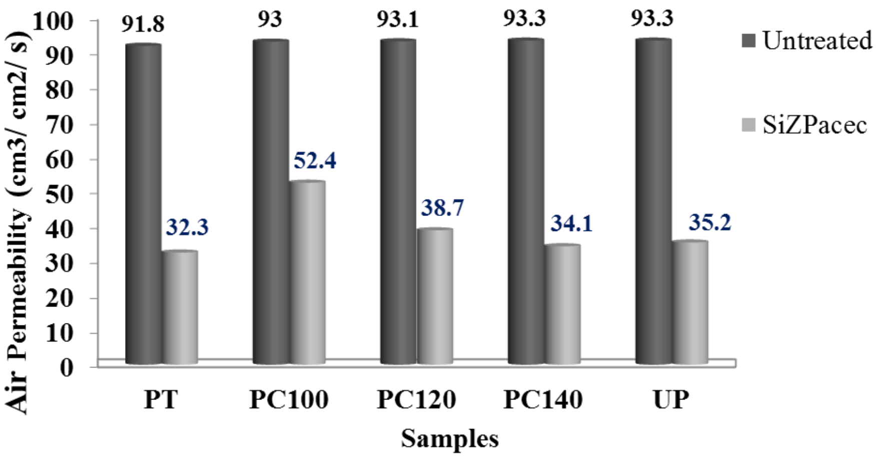


Figure 29. Air permeability of samples before and after treatment.

3.8. Self-cleaning Ability

The self-cleaning ability confirmed the original cotton fabric was not able to self-clean in figure 30. The untreated digital-printed fabric was also not able to self-clean the dirt used to test the self-cleaning ability.

Meanwhile, the superhydrophobic original fabric- S and the digital-printed superhydrophobic fabric-PS had the water droplets on the silicon carbide collected in the droplets and trapped the dirt in the dropplets. When the surface was agitated, the dropplets rolled off from the surfaces leaving very minute particles of the dirt on the surfaces proving more room for improvement for self-cleaning abilities.

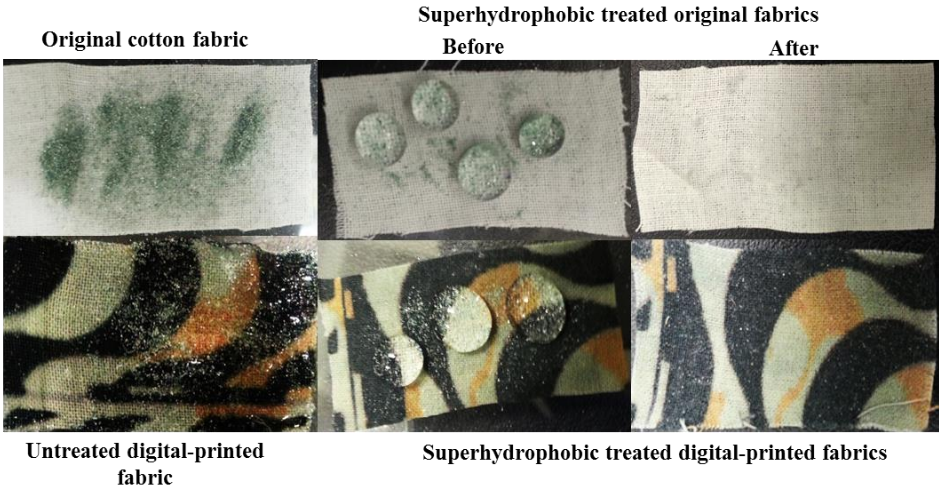


Figure 30. Images showing the self-cleaning abilities of untreated and treated printed fabrics.

Conclusion

In conclusion, the morphology of the superhydrophobic treated digital-printed fabric samples proved that the nanoparticles employed in this study are good hydrophobization agents for excellent surface roughness and wettability with WCA at 162^{o}.

Digital-printed fabric with temperature condition at 120^{o}C only after superhydrophobic treatment as the plain cotton fabrics according to previous report had a great effect on the water contact angle recorded.

Therefore, the breathable, durable, self-healing, and superhydrophobic digital-printed cotton fabric could be applicable in the textile industry that needs the functional and dyed fabrics. But it could not meet criteria as a superhydrophobic surface because of the water shedding angle greater than 10^{o}. This needs to be improved by optimizing the surface roughness and surface energy for more diverse applications in subsequent researches to be conducted.

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Abstract in Korean

의복과 직물이 발수성과 자가세정성능이 필요한 환경에 노출되기에, 이를 위해 의복 및 직물 산업에 적용가능한 초소수성 디지털 날염 면직물이 딥코팅 방법을 통해 개발하였다.

제작된 디지털날염 직물의 표면형태 및 마이크로구조는 주사전자현미경으로 관측하였다. 처리시료의 공기투과도 측정을 통해 투과성능이 있는 것을 확인하였다. 제작된 시료의 코팅내구성 평가는 세탁내구성 평가를 통해 이루어졌다.

시료는 내구성이 있는 것으로 나타났으며, 내구성 평가 후 열처리를 하였는데, 세탁내구성 평가 전 162°의 접촉각을 보이던 시료는 세탁내구성 평가와 열처리 후 그보다는 낮은 156°의 접촉각을 보여 초소수성 디지털날염 면직물이 자가회복성능을 나타내는 것을 확인하였다.

개발된 날염직물의 기울임각(shedding angle)은 처리된 날염 면직물의 달라붙는 성질 때문에 용납되는 최대값인 10° 이상의 결과를

나타내어 기록할 수 없었다. 그렇기에, 이 방법은 발수성과 자가회복 두 가지 성능을 가진 디지털날염직물을 만들었고, 의복과 직물 산업, 특히 패션 악세서리에서 적용될 수 있을 것이다.